VI.9 High Temperature Electrochemistry Center - PNNL

Objectives

The High Temperature Electrochemistry Center provides crosscutting, multidisciplinary research that supports the Office of Fossil Energy's mission to improve the efficiency and minimize the environmental consequences of electrical power generation from fossil fuels.

- Develop reversible solid oxide fuel cell technology capable of efficiently producing hydrogen in an electrolysis mode as well as producing electrical power from stored hydrogen in the fuel cell mode.
- Develop energy storage concepts that utilize electrochemical processes at high temperatures.
- Develop oxide-based thermoelectric materials and forms that can be used to produce electricity from waste heat available from fuel cell systems.
- Investigate how the performance of solid oxide fuel cells may be affected by contaminants present in coal gas.

Accomplishments

- Electrode inefficiencies in reversible fuel cells have been established as a function of temperature, steam, and hydrogen partial pressure. Nickel-based hydrogen electrodes show higher activity in the fuel cell than electrolysis direction, while the opposite was found for titanate/ceria hydrogen electrodes. Interfacial depletion of oxygen vacancies for mixed conducting oxygen electrodes resulted in limiting currents in the electrolysis direction. Full reversible fuel cell stacks showed higher resistances in the electrolysis versus fuel cell direction, consistent with electrode studies.
- An *n*-type oxide material has been developed that exhibits a thermoelectric figure of merit more than three times higher than that of any other known *n*-type bulk oxide and is stable to high temperatures. When coupled with high-yield *p*-type oxides, these new *n*-type materials will enable the development of efficient thermoelectric generators capable of generating electricity from waste heat available from fuel cell systems.
- Densification of lanthanum strontium manganite oxygen electrode materials at substantially lowered temperatures was achieved by both thermal and oxygen partial pressure cycling. Enhanced sintering occurred in the 700-1000°C range, hundreds of degrees cooler than the usual processing temperature for lanthanum manganites. This behavior is the result of a super-stoichiometric oxygen content, which leads to high metal vacancy concentrations in the perovskite lattice.

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Introduction

The High Temperature Electrochemistry Center (HiTEC) brings together researchers from national laboratories and universities to address topics of relevance to solid oxide fuel cells (SOFCs) operating on fuels derived from coal, in support of DOE's Solid State Energy Conversion Alliance (SECA) program. Research performed under HiTEC is intended to be generally of longer term and more fundamental in nature than that conducted by the SECA core technology or industry teams. The National Energy Technology Laboratory, Montana State University, The University of Florida, and the Pacific Northwest National Laboratory (PNNL) currently are contributors to HiTEC.

Specific research topics in energy conversion and storage being addressed by the overall program include high temperature steam electrolysis/reversible fuel cell development, interaction of fuel cell anodes with coal-based contaminants, fundamental studies of reactions at the cathode/electrolyte interface, advanced x-ray studies of buried interfaces, the development of corrosion-inhibiting multilayer film technology, modeling and simulation of ion transport processes, waste heat recovery with oxide-based thermoelectrics, and fuel cell diagnostics and controls. Research conducted by HiTEC will help guide the development of advanced fuel cell materials with superior performance, thereby leading to improved SOFC performance when operated on coal-derived fuels.

Approach

Research activities being conducted at PNNL include topics relevant to reversible fuel cells, high temperature thermoelectric generators to convert waste heat to electricity, energy storage concepts, and investigations of hydrogen electrode interactions with coal-based contaminants. Reversible fuel cells offer the capability of producing hydrogen fuel from steam during periods of excess grid capacity, and converting that hydrogen to electricity during later periods of high demand. Research has been focused on understanding electrode activity and stability issues in high steam partial pressures and other conditions unique to this approach. Limits of stored charge and energy in electrochemical cells with composite electrodes are being investigated as a possible means of improving fuel cell load management. New oxide compositions exhibiting high thermoelectric figures of merit are being developed for possible use in thermoelectric generators capable of operating at high temperatures typical of fossil energy conversion devices. Layered structures are being emphasized as a means of limiting the thermal conductivity while maintaining high thermoelectric yields and high electrical conductivity. Also being investigated are interactions of the hydrogen electrode with contaminants known to be present in coal gas. This research will help establish criteria for cleanup of coal gas intended as fuel for SOFCs.

Research at PNNL is conducted in collaboration with Montana State University and the University of Florida. Joint research activities emphasize the development of a fundamental understanding of reactions and processes that occur at the electrode-electrolyte-gas interface, critical to the operation of a wide range of electrochemical technologies including fuel cells, electrolyzers, sensors, and gas separation membranes. Joint research includes the development of simulation methods, which provide insight on ion and electron transport mechanisms; the structure and thermodynamic properties of vacancy clusters; and oxygen reactions at surfaces and interfaces.

Results

Reversible Fuel Cell Studies. Reversible fuel cells offer a potentially attractive means of energy storage, allowing hydrogen fuel production during periods of excess grid capacity and enabling that chemical energy to be converted to electricity during periods of greater need. Reversible fuel cell stacks were produced from anode-supported cells with a Ni/YSZ anode, a cathode composed of $La_{0.60}Sr_{0.40}Co_{0.20}Fe_{0.80}O_x$, and 7 micron-thick YSZ electrolyte, and tested in both fuel cell and electrolysis modes at various steam partial pressures. Losses were consistently higher in the electrolysis than fuel cell mode, as shown in Figure 1, but were largely independent of the steam partial pressure until greater than 90% conversion.

Half-cell measurements performed for several hydrogen and oxygen electrodes showed inherent differences in performance in the fuel cell and electrolysis directions. The activity of the Ni/YSZ hydrogen electrode was clearly higher in the fuel cell mode, as shown in Figure 2. Current-voltage characteristics are consistent with charge transfer as the rate-limiting step in the fuel cell direction, whereas mass transfer contributions were significant

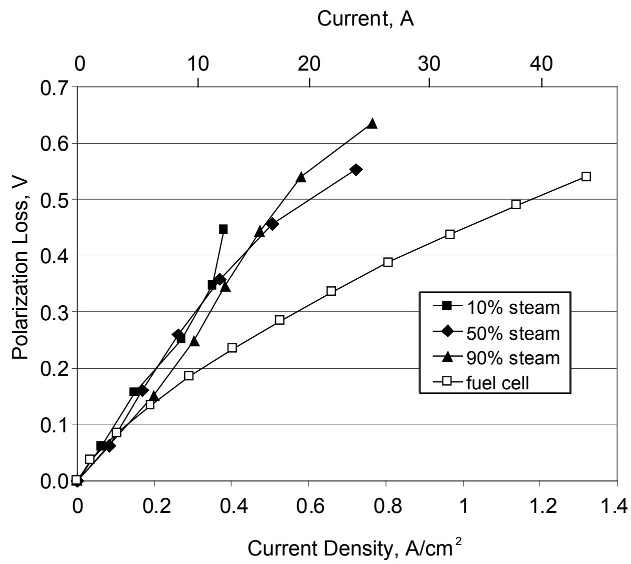

FIGURE 1. Polarization losses versus current density for an anode-supported stack, corrected for initial steam/hydrogen concentrations and reaction at 750°C. The anode was composed of Ni/YSZ, while the cathode was $La_{0.60}Sr_{0.40}Co_{0.20}Fe_{0.80}O_x$. Losses were higher in the electrolysis than fuel cell mode, consistent with the results of half-cell tests.

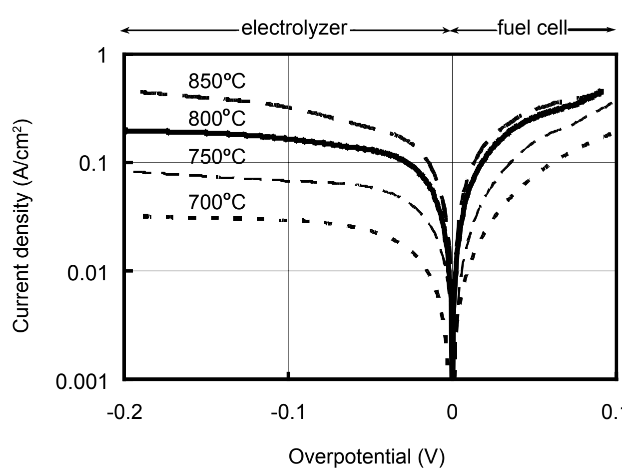

FIGURE 2. Current-overpotential dependencies obtained on Ni-YSZ electrode at $H_2/H_2O/N_2$=10/70/20 in the temperature range 700-850°C, showing higher activity in the fuel cell than electrolyzer direction.

in the electrolysis direction. Titanate-ceria composite hydrogen electrodes were also evaluated and were found to be more active than standard Ni/YSZ compositions for steam electrolysis, whereas the two electrodes show similar activity as the anode in a solid oxide fuel cell. Oxygen electrodes consistently gave higher activity in the fuel cell direction, especially for compositions that exhibit substantial mixed electron and ion conductivity. An example of this behavior is given in Figure 3 for a substituted lanthanum copper ferrite composition. Under cathodic polarization, currents rose more rapidly than expected for charge transfer control, while limiting currents were attained under anodic polarization. This behavior is attributed to the production of oxygen vacancies under cathodic polarization and to the depletion of oxygen vacancies at the interface under anodic polarization. Oxygen electrodes such as lanthanum manganite are not mixed conductors and give much more symmetric anodic and cathodic polarization losses. Though somewhat more resistive in the electrolysis than fuel cell direction, reversible fuel cells appear to be an attractive option for energy storage. If operated above the thermal neutral potential of approximately 1.3 volts per cell, the overall electrolysis reaction is exothermic and the stack can be operated without supplemental heat.

Oxide-Based Thermoelectric Material Development. The thermoelectric properties of layered perovskite materials are being investigated, focusing on *p*-type alkaline earth cobalt oxides and on *n*-type substituted indium oxides. Research on thermoelectric materials involves developing novel synthetic routes to anisotropic materials; determining oxygen nonstoichiometry, particularly associated with transition metal-oxygen planes; and understanding fundamental physics related to anisotropic properties of thermoelectrical power, electrical resistivity, and thermal conductivity. Unlike traditional thermoelectric materials, these oxides are compatible with high temperatures produced in fossil energy conversion systems.

A new *n*-type material consisting of substituted indium oxide has been developed that exhibits a thermoelectric yield more than three times higher than that of any other known bulk oxide. Figure 4 provides figure of merit results for the new material as well as literature results for substituted manganese oxides, which are the best performing *n*-type oxides reported previously. The substituted indium oxide composition shows exceptionally high, metal-like electrical conductivity, greater than 1200 S/cm at 1000°C, and a Seebeck coefficient greater than 110 V/K at that temperature. A small thermoelectric generator consisting of 10 *p*-*n* junctions was constructed by coupling this new *n*-type material with *p*-type layered cobaltites. Such devices would allow waste heat from fuel cells and other fossil energy conversion systems to be converted to electricity.

Enhanced Sintering of Lanthanum Manganite Oxygen Electrodes. In collaboration with the University of Missouri-Rolla, anomalous shrinkage behavior of porous Sr-doped lanthanum manganite ($La_{1-x}Sr_xMnO_{3+\delta}$ or LSM, where x = 0.0 to 0.4) has been studied as a function of thermal cycling, oxygen partial pressure, and Sr dopant concentration. Densification has been observed at temperatures hundreds of degrees lower than the sintering temperature. LSM is an unusual material in that there exists excess oxygen in the lattice in air, actually expressed as an increased number of

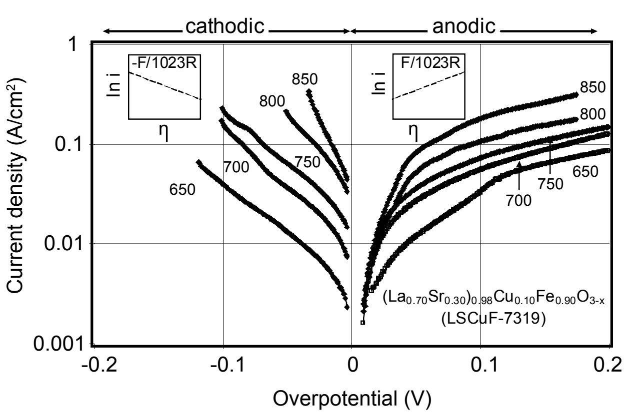

FIGURE 3. Cathodic and anodic overpotentials versus current density for LSCuF-7319 on YSZ with a 3 micron-thick samaria-doped ceria interlayer. Cathodic current densities increased faster than expected for Tafel behavior, while anodic current densities appeared to be reaching a limiting value due to interfacial depletion of oxygen vacancies.

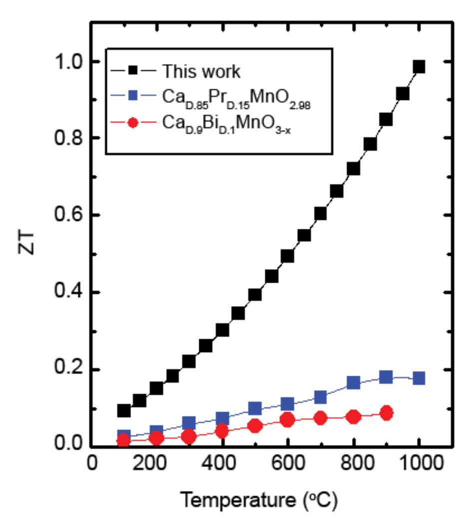

FIGURE 4. Thermoelectric figure of merit versus temperature for n-type bulk oxides. Results for substituted manganese oxides are from Cong et al., Physica B – Cond. Matt. 353, 18 (2004). A new n-type material has been developed with a figure of merit more than three times higher than that of any other known bulk oxide.

metal vacancies. That excess oxygen disappears under conditions possible with cathodic polarization, at about 10^{-3} atm oxygen partial pressure. When cycled between high and low oxygen partial pressures, defects are either created or annihilated to maintain a Schottky equilibrium, resulting in the formation of microscopic voids. These voids can coalesce, eventually leading to densification. This research is pertinent to both the electrochemical and thermal cycling of fuel cells that utilize manganite-based oxygen electrodes.

Conclusions and Future Directions

- Area specific resistances of a reversible fuel cell operating in the electrolysis direction are higher than those in the fuel cell direction, largely due to the performance of the oxygen electrode. Especially for mixed conducting oxygen electrode compositions, depletion of interfacial oxygen vacancies under anodic polarization resulted in lower electrode activity. Nickel-based hydrogen electrodes also showed higher activity in the fuel cell than electrolysis direction, though the opposite was found for titanate/ceria hydrogen electrodes. Future research will focus on electrode and interfacial stability, including those changes induced by repeated changes in the operational mode of a reversible fuel cell.
- A new *n*-type oxide has been identified that exhibits a thermoelectric figure of merit more than three times higher than that of any other known *n*-type bulk oxide and is stable to high temperatures. Previously, only *p*-type oxides with comparable properties had been known. Such materials would enable waste heat available in fossil energy conversion systems to be efficiently converted to electricity. Future research will focus on modifying both the composition and microstructure of this *n*-type material to further enhance its thermoelectric properties.
- Thermal and oxygen partial pressure cycling has been shown to lead to low temperature densification of lanthanum strontium manganite oxygen electrode. This behavior is the result of a super-stoichiometric oxygen content and thus high metal vacancy concentrations unique to the manganite perovskites. Thermal and oxygen partial pressure cycling created temporal gradients in the metal vacancy concentrations, leading to enhanced mobility. Future research on oxygen electrodes will be directed towards the rare earth nickelates, which are unusual in that they contain interstitial oxygen not possible in the perovskite structure.
- Gasified coal contains minor and trace constituents that could impact the stability and performance of a fuel cell system. Investigations will be performed to determine the sensitivity of nickel-based hydrogen electrodes to various coal gas constituents, which will aid in establishing cleanup standards for coal gas intended to supply fuel cells.
- Fundamental studies of the limits of stored charge in high temperature electrochemical cells with composite electrodes will be conducted. Initial studies have achieved capacitances greater than 20 farads per gram and greater than 15 joules per gram active material. Such phenomena may prove useful as a means of electrical energy storage in fuel cell systems. Future studies will include how electrode composition and structure affect stored charge, charge and discharge kinetics, and mechanisms of self-discharge.

Special Recognitions & Awards/Patents Issued

1. PC Rieke, GW Coffey, LR Pederson, OA Marina, JS Hardy, P Singh, and EC Thomsen. Patent Application: US03036800, "Copper-Substituted Perovskite Compositions for Solid Oxide Fuel Cell Cathodes and Oxygen Reduction Electrochemical Devices."

2. OA Marina and LR Pederson. Patent Application US20050250000, "Novel Composite Solid Oxide Fuel Cell Anode Based on Ceria and Strontium Titanate."

FY 2006 Publications/Presentations

1. Radhakrishnan R, Virkar AV, and Singhal SC. "Estimation of charge-transfer resistivity of Pt cathode on YSZ electrolyte using patterned electrodes." J. Electrochem. Soc. 152 (5): A927-A936, 2005.

2. Radhakrishnan R, Virkar AV, and Singhal SC. "Estimation of charge-transfer resistivity of $La_{0.8}Sr_{0.2}MnO_3$ cathode on $Y_{0.16}Zr_{0.84}O_2$ electrolyte using patterned electrodes." J. Electrochem. Soc. 152 (1): A210-A218, 2005.

3. Simner SP, Anderson MD, Xia GG, Yang Z, Pederson LR, and Stevenson JW. "SOFC performance with Fe-Cr-Mn alloy interconnect." J. Electrochem Soc. 152 (4): A740-A745, 2005 (partial support).

4. Simner SP, Anderson MD, Pederson LR, Stevenson JW. "Performance variability of $La(Sr)FeO_3$ SOFC cathode with Pt, Ag, and Au current collectors." J. Electrochem Soc. 152 (9): A1851-A1859 2005 (partial support).

5. Zhou XD, Pederson LR, Cai Q, Yang J, Scarfino BJ, Kim M, Yelon WB, James WJ, Anderson HU, Wang C. "Structural and magnetic properties of $LaMn_{1-x}Fe_xO_3$ $(0 < x < 1.0)$." J. Appl. Phys 99 (8): Art. No. 08M918 2006.

6. Pederson, LR, Singh R, and Zhou X-D. "Application of vacuum deposition methods to solid oxide fuel cells – a review." Vacuum 2006 (in press).

7. Marina OA, Williams MC, Coffey GW, Meinhardt KD, Nguyen CD, Pederson LR, and Thomsen EC. "Electrode performance in reversible solid oxide fuel cells." Revised manuscript submitted to J. Electrochem. Soc. 2006.

8. Marina OA, Pederson LR, Thomsen EC, and Meinhardt KD. "Fuel Electrodes for Reversible Solid Oxide Fuel Cells: Reactivity, Kinetics, and Stability." 30th International Conference on Advanced Ceramics & Composites, Cocoa Beach, Florida, January 2006.

9. Marina OA, Pederson LR, Coffey GW, Thomsen EC, and Meinhardt KD. "Generation of Hydrogen in Reversible Solid Oxide Fuel Cells." 209th Meeting of the Electrochemical Society, Denver, Colorado, May 2006.

10. Zhou X-D, Windisch Jr. CF, Thomsen EC, Cai Q, Hardy JS, Coffey GW, Yang J, Yelon WB, and Pederson LR. "Electrochemical and Structural Properties of Ceramic Protonic Conductors." 209th Electrochemical Society Meeting, Denver, Colorado, May 2006.

11. Hardy JS, Canfield NL, Crum JV, Bandyopadhyay A, Weil KS, and Pederson LR. "Co-Synthesis of Mixed-Conducting Composites for Hydrogen Separation: Compositional Considerations." TMS Annual Meeting and Exposition, San Antonio, Texas, March 2006 (invited).